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Selenium-containing heterocycles from isoselenocyanates: Base-catalyzed reaction of malononitrile with phenyl isoselenocyanate and bromoacetonitrile or alpha-halogenated ketones

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Selenium-Containing Heterocycles from Isoselenocyanates: Base-Catalyzed Reaction of Malononitrile with Phenyl Isoselenocyanate and Bromoacetonitrile or α -Halogenated Ketones

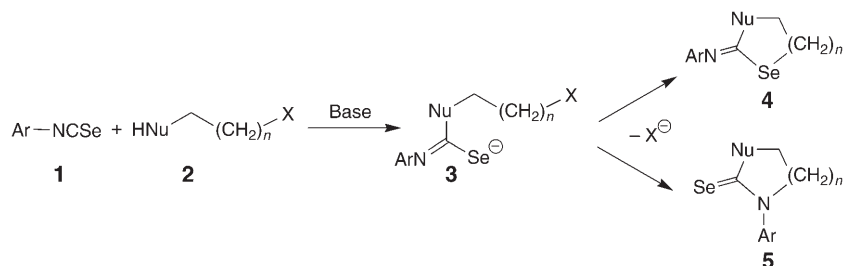
by Geoffroy L. Sommen¹⁾, Anthony Linden, and Heinz Heimgartner*

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The reaction of phenyl isoselenocyanate (**1a**) with malononitrile (propanedinitrile) in DMF in the presence of Et₃N leads to the intermediate ketene N,Se hemiacetal **6a**, which can be trapped with bromoacetonitrile or α halogenated ketones **12a** and **12b** (Scheme 3). The products are [(alkylseleno) (phenylamino)methylene]malononitriles **10** and **13**, which are obtained in good yield. In the case of the (2 oxoalkyl)seleno derivatives **13**, they are in equilibrium with the cyclic hemiacetals **14**. Chemical and spectroscopic evidence for the structures of the new compounds are described. The structure of **14a** was established by X ray crystallography.

1. Introduction. – In the last few years, it has been shown that isoselenocyanates **1** are versatile building blocks for the synthesis of selenium-containing heterocycles [1 – 4] and heterocyclic selones (see [5 – 6] and refs. cit. therein). For example, the reaction of **1** with nucleophiles of type **2**, which also bear an electrophilic group, in the presence of a base gave either Se-containing heterocycles **4** with an imino group or N-containing heterocycles **5** with a selenoxo group (Scheme 1). A likely intermediate is **3**, which undergoes a 5- or 6-*exo-tet* cyclization [7] via the Se- and N-atom, respectively.

Scheme 1

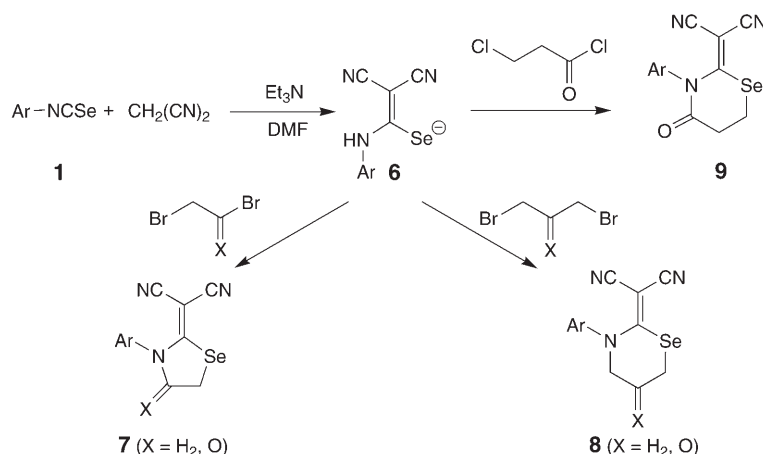


Recently, we have shown that ‘three-component reactions’ of **1**, cyanomethylene derivatives, and bis-electrophiles in the presence of a base yield 2-methylene-1,3-

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selenazolidine [8] and analogous 1,3-selenazinane (=tetrahydro-1*H*-1,3-selenazine) derivatives [9] (Scheme 2). For example, the reactions with 1,2-dibromoethane or 2-bromoacetyl bromide yield **7**, and the analogous reactions with 1,3-dibromopropane, 1,3-dichloroacetone, and 3-chloropropanoyl chloride, respectively, give the six-membered products **8**²⁾ or **9**. The crucial intermediate of these reactions is the N,Se-hemiacetal **6**, which in all cases reacted with the bis-electrophilic reagent by double nucleophilic substitution.

Scheme 2



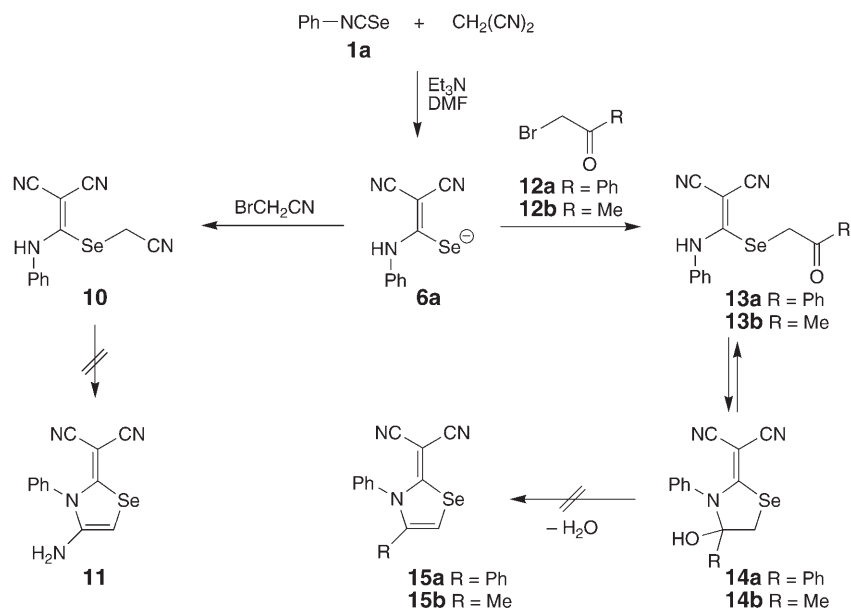
With the aim of further extending this concept, we carried out reactions of **1a** (Ar = Ph), malononitrile, and α -halogenated ketones or bromoacetonitrile.

2. Results and Discussion. – By following the previously described procedure [8][9], the intermediate **6a** was generated *in situ* by treatment of a mixture of malononitrile and phenyl isoselenocyanate (**1a**) in DMF with an equimolar amount of Et₃N at room temperature (Scheme 3). After reaction with bromoacetonitrile, a brownish solid was isolated. On the basis of the spectroscopic data, structure **10** was assigned to this product. Obviously, **6a** underwent an S_N2 reaction with bromoacetonitrile, but no subsequent cyclization to the expected (4-amino-1,3-selenazol-2(3*H*)-ylidene)malononitrile **11** occurred (Scheme 3). All attempts to obtain a cyclized product by treatment of **10** with different bases failed and led to the decomposition of **10**.

The CI MS of **10** shows the base peak at *m/z* 306, and the elemental analysis corresponds with the molecular formula C₁₂H₈N₄Se, *i.e.*, a product, which was formed by a substitution reaction of **6a** and bromoacetonitrile. According to the IR and ¹³C NMR spectra, the product contains three CN groups (2212, 2201, and 2194 cm⁻¹, and δ (C) 115.1, 114.9, and 110.1, resp.). In the ¹H NMR spectrum, a CH₂ group absorbs at δ (H) 4.38 as a s, and a broad s at δ (H) 13.85 can be attributed to a NH group.

²⁾ The crystal structure of **8** (Ar = 4-Cl-C₆H₄, X = O) [9] was established also by X ray crystallography (see below, Fig. and Table).

Scheme 3



In the analogous reaction of **1a** with malononitrile and α -bromoacetophenone (**12a**) or α -bromoacetone (**12b**), respectively (Scheme 3), the products were isolated as pale yellow crystals. Their data were consistent with the products of a substitution reaction of the intermediate **6a** and the α -halogenated ketone **12**, but inconsistent with the desired products **15** (Scheme 3). The IR data excluded ketone derivatives **13**; however, the NMR and MS data were compatible with structures **13** and 1,3-selenazolidine derivatives **14**. Taking also the X-ray analyses (see below) into account, we propose that the products which were obtained from **1a**, malononitrile, and α -halogenated ketones **12** exist in the keto form **13** in solution but as the cyclic ‘hemiacetal’ **14** in the crystalline state. Again, treatment of **13a/14a** with a base did not result in the elimination of H_2O to give the desired compound **15a** but in the decomposition of the product.

In the IR spectrum (KBr), the products from **6a** and **12** show two signals for CN groups and a broad absorption at $3370\text{--}3400\text{ cm}^{-1}$, but no C=O absorption. The ^{13}C NMR spectra indicate clearly the presence of a C=O group ($\delta(\text{C})$ 196.5 and 206.0 for the products from **12a** and **12b**, resp.). Furthermore, in the ^1H NMR spectra, a s for a CH_2 group appears at $\delta(\text{H})$ 3.69 and 3.64, respectively ($\delta(\text{C})$ 34.2 and 36.7 in the ^{13}C NMR spectra). The CI MS and elemental analyses are in accordance with products **13** or 1,3-selenazolidines **14** but not with **15**.

Finally, the structure of **14a** was established by an X-ray crystal-structure determination (Fig.). In the crystal structure of **14a**, the five-membered ring has an envelope conformation with atom C(5) as the envelope flap. Most of the geometric parameters are similar to those of the previously described structures of (1,3-

selenazolidin-2-ylidene)malononitriles **7** and a (1,3-selenazinan-2-ylidene)malononitrile **9** [8][9]: the two CN groups are almost coplanar with the atoms Se(1), C(2), N(3), and C(6), the C(2)=C(6) bond is longer (1.389(3) Å) than a normal C=C bond, whereas the formal single bonds Se(1)–C(2), N(3)–C(2), C(6)–C(7), and C(6)–C(8) are short (1.894(2), 1.332(3), 1.424(3), and 1.428(3) Å, resp.). Furthermore, the bond angle C(2)–C(6)–C(8) is larger than normal at 125.9(2)°, whereas the angles C(2)–C(6)–C(7) and C(7)–C(6)–C(8) are small (117.7(2) and 116.4(2)°, resp.), *i.e.*, the CN(8) group is tilted away from the PhN(3) residue. The OH group forms an intermolecular H-bond with one of the cyano N-atoms of a neighboring molecule. These interactions link the molecules into extended chains, which run parallel to the [001] direction and can be described by a graph set motif [11] of C(8).

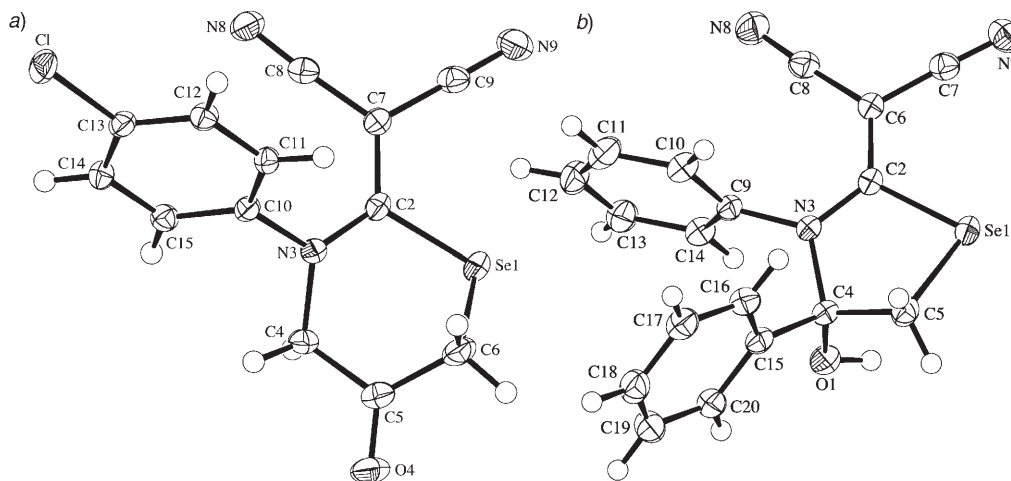


Figure. ORTEP Plots [10] of the molecular structures of a) **8** (Ar = 4-Cl-C₆H₄, X = O) and b) **14a**. Arbitrary atom numbering; 50% probability ellipsoids.

The heterocycle of **8** (Ar = 4-Cl-C₆H₄, X = O) [9] has a distorted screw-boat conformation as shown by its crystal structure (*Fig.*). The geometric parameters are again mostly similar to those of **7**, **9**, and **14** (*e.g.*, a long C(2)=C(7) bond (1.385(3) Å) and short Se(1)–C(2), N(3)–C(2), C(7)–C(8), and C(7)–C(9) bonds (1.890(2), 1.351(2), 1.432(3), and 1.427(3) Å, resp.), as well as a tilting of the CN(8) group away from the aromatic residue (the bond angle C(2)–C(7)–C(8) is 124.9(2)° and C(8)–C(7)–C(9) is 115.1(2)°). In contrast, however, the environment about the C=C bond is not planar, the plane defined by atoms C(7), C(8), and C(9) making an angle of 14.3(3)° with the plane defined by atoms N(3), C(2) and Se(1).

In conclusion, the three-component reaction of **1a**, malononitrile, and bromoacetone nitrile or α -halogenated ketones leads to the acyclic adducts **10** and **13**, respectively, in good yield *via* the intermediate **6a**. The ketone derivatives of type **13** are in equilibrium with the 1,3-selenazolidine derivatives **14**, which can be isolated in the crystalline form.

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Experimental Part

1. *General.* See [12][13]. TLC: silica gel 60 F_{254} plates (0.25 mm; Merck). Column chromatography (CC): silica gel 60 (0.040–0.063 mm; Merck). M.p.: Büchi B 540 apparatus, in capillaries; uncorrected. IR Spectra: Perkin Elmer 1600 FT IR spectrophotometer; in KBr; ν in cm^{-1} . ^1H (300 MHz) and ^{13}C NMR (75.5 MHz) Spectra: Bruker ARX 300 instrument; in CDCl_3 ; chemical shifts δ in ppm, J in Hz. CI MS: Finnigan SSQ 700 or MAT 90 instrument; NH_3 as carrier gas; in m/z .

2. *Starting Materials.* Propanedinitrile (malononitrile) and all halogenated compounds are commercially available (Fluka). Phenyl isoselenocyanate (**1a**) was prepared according to Barton's procedure starting from formanilide [14], which is commercially available (Fluka, Aldrich).

3. *Reaction of 1a, Malononitrile, and a Halogenated Compound: General Procedure.* To a soln. of malononitrile (73 mg, 1.1 mmol) in DMF (10 ml), Et_3N (0.15 ml, 1.1 mmol) was added, and the mixture was stirred for 30 min at r.t. Then, **1a** (200 mg, 1.1 mmol) was added, and the mixture was stirred for 1 h at r.t. The halogenated compound (1.1 mmol) was added dropwise, the mixture stirred for 4 h, and the solvent evaporated. The crude product was purified by CC (hexane/AcOEt mixtures).

2 $\{[(\text{Cyanomethyl})\text{seleno}](\text{phenylamino})\text{methylene}\}\text{propanedinitrile}$ (**10**). From **1a**, malononitrile, and bromoacetonitrile: 234 mg (74%) of **10**. Brownish crystals. M.p. 166–168° (AcOEt/hexane). IR (KBr): 2212s, 2201s, 2194s, 1596w, 1554w, 1523s, 1488w, 1454m, 1415w, 1388w, 1354m, 1212w, 1200w, 1166w, 1105w, 1054w, 1022w, 1008w, 912w, 905w, 888w, 754w, 736w, 705w, 698m. ^1H NMR: 4.38 (s, CH_2); 7.40–7.45 (m, 2 arom. H); 7.50–7.57 (m, 3 arom. H); 13.85 (br. s, NH). ^{13}C NMR: 29.1 (CH_2); 57.8 ($\text{C}(\text{CN})_2$); 110.1, 114.9, 115.1 (3 CN); 128.9 (2 arom. CH); 129.4 (2 arom. CH); 130.8 (1 arom. CH); 134.8 (1 arom. C); 173.3 (CNSe). CI MS: 306 (100, $[M(^{80}\text{Se}) + \text{NH}_4]^+$), 289 (10, $[M(^{80}\text{Se}) + 1]^+$). Anal. calc. for $\text{C}_{12}\text{H}_8\text{N}_4\text{Se}$ (287.18): C 50.19, H 2.81, N 19.51; found: C 49.95, H 3.02, N 19.63.

2 $\{[(2\text{-Oxo-2-phenylethyl})\text{seleno}](\text{phenylamino})\text{methylene}\}\text{propanedinitrile}$ (**13a**)/2 (4-Hydroxy-3,4-diphenyl-1,3-selenazolidin-2-ylidene)propanedinitrile (**14a**). From **1a**, malononitrile, and α -bromoacetophenone (**12a**): 326 mg (81%) of **14a**. Yellowish crystals. M.p. 155–157° (AcOEt/hexane). IR (**14a**; KBr): 3397s, 3055w, 2211s, 2196s, 1598w, 1554w, 1518s, 1490m, 1450m, 1421w, 1392w, 1346m, 1212m, 1198w, 1168w, 1105w, 1075w, 1031w, 1015m, 1003w, 984w, 931w, 907w, 852w, 764w, 737w, 707w, 694m. ^1H NMR (**13a**): 3.69 (s, CH_2); 6.76 (d, J 7.9, 1 arom. H); 7.03 (d, J 8.1, 1 arom. H); 7.12–7.25 (m, 6 arom. H); 7.44 (t, J 8.1, 2 arom. H); 10.68 (br. s, NH). ^{13}C NMR (**13a**): 34.2 (CH_2); 49.8 ($\text{C}(\text{CN})_2$); 111.9, 118.2 (2 CN); 126.0 (1 arom. CH); 126.5 (2 arom. CH); 127.8 (2 arom. CH); 128.3 (2 arom. CH); 128.5 (2 arom. CH); 129.3 (1 arom. CH); 137.1, 139.6 (2 arom. C); 172.6 (CNSe); 196.5 (CO). CI MS (**14a**): 385 (100, $[M(^{80}\text{Se}) + \text{NH}_4]^+$), 368 (10, $[M(^{80}\text{Se}) + 1]^+$). Anal. calc. for $\text{C}_{18}\text{H}_{13}\text{N}_3\text{OSe}$ (366.28): C 59.02, H 3.58, N 11.47; found: C 58.91, H 3.58, N 11.47.

2 $\{[(2\text{-Oxopropyl})\text{seleno}](\text{phenylamino})\text{methylene}\}\text{propanedinitrile}$ (**13b**)/2 (4-Hydroxy-4-methyl-3-phenyl-1,3-selenazolidin-2-ylidene)propanedinitrile (**14b**). From **1a**, malononitrile, and α -bromoacetone (**12b**): 221 mg (66%) of **14b**. Pale yellow crystals. M.p. 170–172° (AcOEt/hexane). IR (**14b**; KBr): 3371s, 2212s, 2197s, 1595w, 1507s, 1454w, 1428w, 1392w, 1348m, 1225w, 1181w, 1161w, 1105w, 1054m, 999w, 953w, 903w, 851w, 744w, 694m. ^1H NMR (**13b**): 1.31 (s, Me); 3.64 (s, CH_2); 7.26–7.31 (m, 2 arom. H); 7.39–7.49 (m, 3 arom. H); 11.45 (br. s, NH). ^{13}C NMR (**13b**): 25.8 (Me); 36.7 (CH_2); 47.7 ($\text{C}(\text{CN})_2$); 112.0, 118.2 (2 CN); 129.0 (2 arom. CH); 129.7 (2 arom. CH); 130.0 (1 arom. CH); 136.5 (1 arom. C); 171.7 (CNSe); 206.2 (CO). CI MS (**14b**): 323 (100, $[M(^{80}\text{Se}) + \text{NH}_4]^+$), 305 (31, $[M(^{80}\text{Se}) + 1]^+$). Anal. calc. for $\text{C}_{13}\text{H}_{11}\text{N}_3\text{OSe}$ (304.21): C 51.33, H 3.64, N 13.81; found: C 51.28, H 3.71, N 13.68.

4. *X-Ray Crystal Structure Determination of 8* (Ar = 4-Cl- C_6H_4 , X = O) and **14a** (see Table and Fig.)³⁾. All measurements were made on a Nonius KappaCCD diffractometer [15] by using graphite

³⁾ CCDC 647556 and 647557 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.ac.uk/data_request/cif.

monochromated MoK α radiation (λ 0.71073 Å) and an Oxford Cryosystems Cryostream 700 cooler. Data reduction was performed with HKL Denzo and Scalepack [16]. The intensities were corrected for Lorentz and polarization effects, and an absorption correction based on the multi scan method [17] was applied. Equivalent reflections were merged. Data collection and refinement parameters are given in the Table, and views of the molecules are shown in the Figure. The structure of **8** (Ar 4 Cl C₆H₄, X O) was solved by direct methods with SIR92 [18], which revealed the positions of all non H atoms. The non H atoms were refined anisotropically. The structure of **14a** was solved by heavy atom Patterson methods [19], which revealed the position of the Se atom. All remaining non H atoms were located in a Fourier expansion of the Patterson solution, which was performed by DIRDIF 94 [20]. Non H atoms were refined anisotropically. The hydroxy H atom of **14a** was placed in the position indicated by a difference electron density map and its position was allowed to refine together with an isotropic displacement parameter. All remaining H atoms and all H atoms of **8** (Ar 4 Cl C₆H₄, X O) were placed in geometrically calculated positions and refined with a riding model where each H atom was assigned a

Table. Crystallographic Data for Compounds **8** (Ar 4 Cl C₆H₄, X O) and **14a**

	8 (Ar 4 Cl C ₆ H ₄ , X O)	14a
Crystallized from	MeCN	AcOEt/hexane
Empirical formula	C ₁₃ H ₈ ClN ₃ OSe	C ₁₈ H ₁₃ N ₃ OSe
M_r	336.58	366.22
Crystal color, habit	yellow, prism	colorless, prism
Crystal dimensions [mm]	0.07 × 0.20 × 0.27	0.23 × 0.23 × 0.25
Temperature [K]	160(1)	160(1)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$C2/c$
Z	4	8
Reflections for cell determination	18890	218336
2θ range for cell determination [°]	4–60	4–60
Unit cell parameters: a [Å]	9.9940(2)	33.263(1)
b [Å]	12.2053(2)	6.6722(2)
c [Å]	11.4240(2)	14.6996(4)
β [°]	111.419(1)	109.014(2)
V [Å ³]	1297.25(4)	3084.4(2)
D_x [g cm ⁻³]	1.723	1.577
μ (MoK α) [mm ⁻¹]	3.092	2.441
Scan type	ϕ and ω	ϕ and ω
$2\theta_{\text{max}}$ [°]	60	60
Transmission factors [min; max]	0.567; 0.811	0.498; 0.592
Total reflections measured	32822	37952
Symmetry independent reflections	3786	4516
Reflections with $I > 2\sigma(I)$	3104	3627
Reflections used in refinement	3786	4516
Parameters refined	173	213
Final $R(F)$ ($I > 2\sigma(I)$ reflections)	0.0310	0.0410
$wR(F^2)$ (all data)	0.0754	0.0993
Weighting parameters [a ; b] ^{a)}	0.0338; 0.7475	0.0479; 2.9032
Goodness of fit	1.046	1.102
Secondary extinction coefficient	0.0024(6)	0.0052(3)
Final $\Delta_{\text{max}}/\sigma$	0.001	0.004
$\Delta\rho$ (max; min) [e Å ⁻³]	0.59; 0.68	0.61; 0.75

^{a)} $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = (F_o^2 + 2F_c^2)/3$

fixed isotropic displacement parameter with a value equal to $1.2U_{\text{eq}}$ of its parent C atom. The refinement of each structure was carried out on F^2 by using full matrix least squares procedures, which minimized the function $\sum w(F_o^2 - F_c^2)^2$. Corrections for secondary extinction were applied. Neutral atom scattering factors for non H atoms were taken from [21a], and the scattering factors for H atoms were taken from [22]. Anomalous dispersion effects were included in F_c [23]; the values for f' and f'' were those of [21b]. The values of the mass attenuation coefficients are those of [21c]. All calculations were performed with the SHELXL97 [24] program.

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